Isotopes and Atomic Weights.[1]

By DR. F. W. ASTON.

POSSIBLY the most important generalisation in the whole history of chemistry is the atomic theory put forward by John Dalton in 1803, and it is a striking tribute to the shrewd intuition of that observer that of his five postulates only one seems to be in the least degree faulty, and more than a century of active and unremitting investigation has been necessary to detect the flaw in that.

The postulate in question states that "atoms of the same element are similar to one another and equal in weight." Of course, if we take this as a definition of the word "element," it becomes a truism; but, on the other hand, what Dalton meant by an element and what we understand by the word to-day is a substance such as hydrogen, oxygen, chlorine, or lead, which has unique chemical properties, and cannot be resolved into more elementary constituents by any known chemical process. For many of the well-known elements Dalton's postulate still appears to be strictly true, but for others, probably the majority, it needs some modification.

The general state of opinion at the end of last century may be gathered from the following quotations from Sir William Ramsay's address to the British Association at Toronto in 1897:

> There have been almost innumerable attempts to reduce the differences between atomic weights to regularity by contriving some formula which will express the numbers which represent the atomic weights with all their irregularities. Needless to say, such attempts have in no case been successful. Apparent success is always attained at the expense of accuracy, and the numbers reproduced are not those accepted as the true atomic weights. Such attempts, in my opinion, are futile. Still, the human mind does not rest contented in merely chronicling such an irregularity; it strives to understand why such an irregularity should exist. . . . The idea . . . has been advanced by Prof. Schützenberger, and later by Mr. Crookes, that what we term the atomic weight of an element is a mean; that when we say the atomic weight of oxygen is 16, we merely state that the average atomic weight is 16; and it is not inconceivable that a certain number of molecules have a weight somewhat higher than 32, while a certain number have a lower weight.

That such conjectures were then regarded as wildly speculative shows how strong was the faith in Dalton's postulate, which is all the more remarkable when we consider that at that time not one single direct experimental proof of it had been offered. Such proof, obviously, can be obtained only by some method which measures the masses of atoms individually, and at that time none had been developed.

The first direct evidence that the atoms of an element were, at least approximately, equal in mass appears to be that obtained by Sir J. J. Thomson in 1910 by his well-known method of analysis of positive rays. The fact that sharply defined parabolic streaks were obtained at all proves that the ratio of the masses of the separate particles causing them to the charges of electricity they carry is constant. The latter was known to be a definite unit, or a simple multiple of it, so that if the masses of the individual atoms varied amongst each other in an arbitrary manner, an indistinct blur would result instead of a clear-cut parabola.

Before going on to consider the evidence of positive rays in greater detail, it will be as well to re-state briefly the evidence upon which the theory of isotopes was founded. The first indication that it might be possible to obtain substances having identical chemical properties, but different atomic weights, was afforded by the brilliant researches on the radio-active elements made by Sir E. Rutherford and his colleagues. Investigations on the transformations of the different radioactive families showed that certain products, such as lead, could be formed in several ways. Each of the leads so formed was found to have chemical properties identical in every respect with those of ordinary lead, but their method of production precluded any possibility of them all having the same atomic weight. Such bodies, although having different atomic weights, must occupy the same position in the periodic table of the elements, and on this account have been called "isotopes" by Prof. Soddy.

Moseley's epoch-making discovery has shown us that chemical properties depend, not upon atomic weight, but upon something much more fundamental, namely, *atomic number.* The atomic number of an element is the number of units of positive electricity on the nucleus of its atoms; the nuclear charge of hydrogen is 1, of helium 2, of lithium 3, and so on. We see, therefore, that isotopes are elements having the same atomic number, but different atomic weights.

The theory of isotopes was triumphantly vindicated during the war by the researches of Soddy, Richards, Hönigschmid, and others on the atomic weights of lead found in various radioactive minerals. Quantities were obtainable which were ample for the most accurate determinations by chemical methods, and the atomic weights were found to differ from each other and from ordinary lead by quantities altogether outside possible experimental error. Long before this convincing proof was forthcoming, the theory of isotopes was discussed with the greatest interest in connection with atomic weights in general. If isotopes occurred among the heavy elements, why should they not be possible among the lighter non-radio-active ones, in which case elements with fractional atomic weights might clearly be mixtures, the constituents having atomic weights equal to whole numbers? This explanation was a very attractive one, for the curious jumble of whole numbers and fractions in the atomic weights when referred to oxygen as 16 has always been a serious stumbling-block in the way of any simple theory of atom-building. The accurately determined atomic weight of chlorine, 35·46, has certainly nothing to recommend it. It is reminiscent of the number of square yards in a square rod, pole, or perch; but the idea of Nature working on the same lines as the British weights and measures is eminently unattractive.

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[1] Discourse delivered at the Royal Institution on Friday, February 11.

The first support of the isotope theory among non-radio-active elements was given by the anomalous behaviour of the inactive gas neon when analysed by Sir J. J. Thomson's method of positive rays. It is of interest to note that the announcement was made in this room by Sir J. J. Thomson himself, and that the first sample of gas to show the effect was supplied by Sir James Dewar. This peculiarity was that whereas all elements previously examined gave single, or apparently single, parabolas, that given by neon was definitely double. The brighter curve corresponded roughly to an atomic weight of 20, the fainter companion to one of 22, the atomic weight of neon being 20·20. In consequence of reasoning adduced from the characteristics of the line 22, the discoverer was of the opinion that it could not be attributed to any compound, and that therefore it represented a hitherto unknown elementary constituent of neon. This agreed very well with the idea of isotopes which had just been promulgated, so that it was of great importance to investigate the point as fully as possible.

The first line of attack was an attempt at separation by repeated fractionation over charcoal cooled with liquid air, but, even after many thousands of operations, the result was entirely negative. It is some satisfaction to know that this result was inevitable, as Prof. Lindemann has recently shown on thermodynamical grounds. Fractional diffusion through pipeclay was more effective, and gave a positive result. An apparent difference of density of 0·7 per cent. between the lightest and heaviest fractions was obtained after an exceedingly laborious set of operations. When the war interrupted the research, it might be said that several independent lines of reasoning pointed to the idea that neon was a mixture of isotopes, but that none of them could be said to carry the conviction necessary in such an important development.

When the work was recommenced, attention was again turned towards positive rays, for it was clear that if an analysis could be made with such accuracy that it could be demonstrated with certainty that neither of the two atomic weights so determined agreed with the accepted chemical figure, the matter could be regarded as settled. This could not be done with the parabolas already obtained, but the accuracy of measurement was raised to the required degree by means of the arrangement illustrated in Fig. 1. Positive rays are sorted out into a thin ribbon by means of the two parallel slits $S_1 S_2$, and are then spread into an electric spectrum by means of the charged plates $P_1 P_2$. A portion of this spectrum deflected through an angle θ is selected by the diaphragm D and passed between the circular poles of a powerful electromagnet O the field of which is such as to bend the rays back again through an angle ϕ more than twice as great as θ. The result of this is that rays having a constant mass (or, more correctly, constant m/e) will converge to a focus F, and if a photographic plate is placed at GF, as indicated, a *spectrum dependent on mass alone* will be obtained. On account of its analogy to optical apparatus, the instrument has been called a positive-ray spectrograph, and the spectrum produced a mass-spectrum.

Fig. 2 shows a number of typical mass-spectra obtained by this means. The numbers above the lines indicate the masses they correspond to on the scale O = 16. It will be noticed that the displacement to the right with increasing mass is roughly linear. The measurements of mass made are not absolute, but relative to lines which correspond to known masses. Such lines, due to hydrogen, carbon, oxygen, and their compounds, are generally present as impurities, or purposely added, for pure gases are not suitable for the smooth working of the discharge tube. The two principal groups of these reference lines are the C_1 group due to C(12), CH(13), CH_2(14), CH_3(15), CH_4 or O (16), and the C_2 group (24 to 30) containing the very strong line C_2H_4 or CO (28). These groups will be seen in several of the spectra reproduced, and they give, with the CO_2 line (44), a very good scale of reference.

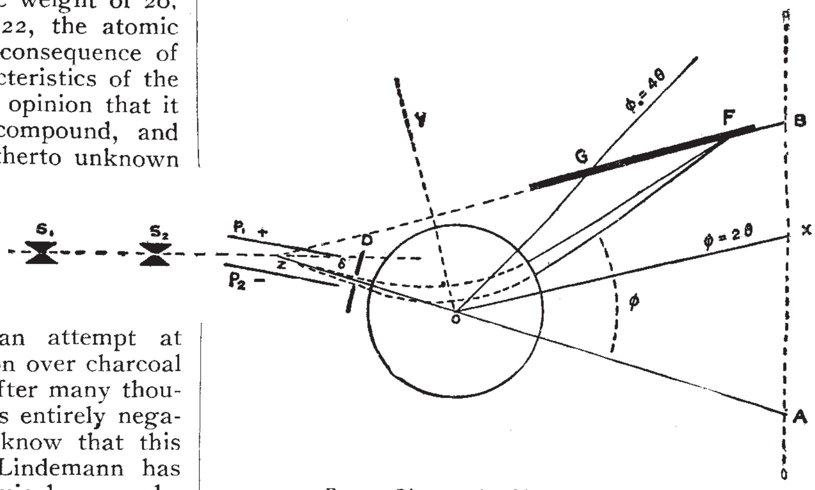

FIG. 1.—Diagram of positive-ray spectrograph.

It must be remembered that the ratio of mass to charge is the real quantity measured by the position of the lines. Many of the particles are capable of carrying more than one charge. A particle carrying two charges will appear as having half its real mass, one carrying three charges as if its mass were one-third, and so on. Lines due to these are called lines of the second and third order. Lines of high order are particularly valuable in extending our scale of reference.

When neon was introduced into the apparatus four new lines made their appearance at 10, 11, 20, and 22. The first pair are second-order lines, and are fainter than the other two. All four are well placed for direct comparison with the standard lines, and a series of consistent measurements showed that to within about one part in a thousand the atomic weights of the isotopes composing neon are 20·00 and 22·00 respectively. Ten per cent. of the latter would bring the mean atomic weight to the accepted value of 20·20, and the relative intensity of the lines agrees well with this proportion. The isotopic constitution of neon seems, therefore, settled beyond all doubt.

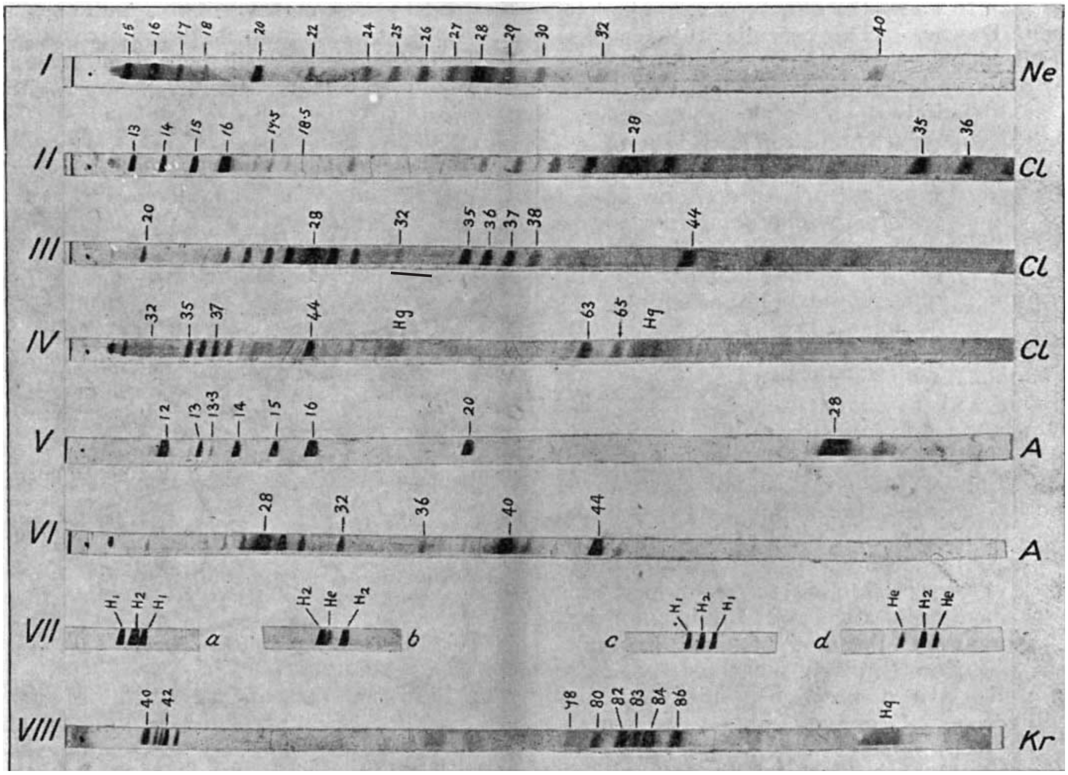

FIG. 2.—Typical mass-spectra.

The element chlorine was naturally the next to be analysed, and the explanation of its fractional atomic weight was obvious from the first plate taken. Its mass-spectrum is characterised by four strong first-order lines at 35, 36, 37, 38, with fainter ones at 39, 40. There is no sign whatever of any line at 35·46. The simplest explanation of the group is to suppose the lines 35 and 37 are due to the isotopic chlorines, and lines 36 and 38 to their corresponding hydrochloric acids. The elementary nature of lines 35 and 37 is also indicated by the second-order lines at 17·5, 18·5, and also, when phosgene was used, by the appearance of lines at 63, 65, due to $COCl^{35}$ and $COCl^{37}$.

Quite recently it has been found possible to obtain the spectrum of negatively charged rays. These rays are formed by a normal, positively charged ray picking up two electrons. On the negative spectrum of chlorine only two lines, 35 and 37, can be seen, so that the lines at 36 and 38 cannot be due to isotopes of the element. These results, taken with many others which cannot be stated here in detail, show that chlorine is a complex element, and that its principal isotopes are of atomic weight 35 and 37. There may be, in addition, a small proportion of a third of weight 39, but this is doubtful. Spectra II., III., and IV. show the results with chlorine taken with different magnetic field strengths.

The objection has been raised on many occasions that if chlorine consists of isotopes, how is it that its atomic weight has been determined so accurately and so consistently by different chemists? The obvious explanation of this appears to be that all the accurate determinations have been done with chlorine derived originally from the same source—the sea—which has been perfectly mixed for æons. If samples of the element are obtained from some other original source, it is quite possible that other values of atomic weight will be determined, exactly as in the case of lead.

The mass-spectrum of argon shows an exceedingly bright line at 40, with second-order line at 20, and third-order line at $13\frac{1}{3}$. The last is particularly well placed between known reference lines, and its measurement showed that the triply charged atom causing it had a mass 40·00 very exactly. Now the accepted atomic weight of argon is less than 40, so the presence of a lighter isotope was suggested. This was found at 36, and has now been fully substantiated; its presence to the extent of about 3 per cent. is sufficient to account for the mean atomic weight obtained by density determinations.

The elements hydrogen and helium presented peculiar difficulties, as their lines were too far removed from the reference lines for direct comparison. By means of a special "bracketing" method, moderately accurate values were obtained. Helium appears to be exactly 4 on the oxygen scale, but hydrogen is definitely greater than unity. The value obtained agrees very well with that already arrived at by chemical methods—namely, 1·008. At the same time, measurements of the 3 line, first observed by Sir J. J. Thomson, were made which came out at 3·024, satisfactorily proving it to be due to triatomic hydrogen.

Krypton and xenon gave surprisingly complex results, the former consisting of six isotopes 78, 80, 82, 83, 84, 86. The weights of these could be determined with great accuracy by means of the excellent second- and third-order lines they gave. The first experiments with xenon led to the observation of five isotopes, the provisional values of which were given as one unit too low. Owing to the kindness of Prof. Travers and Dr. Masson, I have recently been enabled to repeat the analysis with gas much richer in xenon. With this the second-order lines could be observed and measured. The five principal isotopes of xenon are 129, 131, 132, 134, 136; there is apparently a faint sixth component at 128, and a doubtful seventh at 130.

Experiments with boron fluoride indicated that boron has at least two isotopes, 10 and 11, and that fluorine is a simple element of atomic weight 19.

Silicon is another unmistakably complex element having two isotopes, 28 and 29, with a possible additional one, 30.

Bromine was of great interest. As it has an atomic weight almost exactly 80, it might reasonably be expected to be simple and an isobare of one of the kryptons; actually it consists of equal parts of 79 and 81.

Sulphur, phosphorus, and arsenic are all apparently simple elements. Mercury is certainly complex, though its closer components cannot be resolved with the present apparatus. Its very characteristic groups are seen as high as the fifth order, and appear on nearly all the spectra taken. The group consists of a continuous succession of lines forming a band 197 to 200, a strong line at 202, and a weak one at 204. Recently at Copenhagen Brönsted and Hevesy have succeeded in partially separating the isotopes of mercury by a fractional distillation at extremely low pressure. They give as their figures for the densities compared with normal mercury as unity:—

Condensed mercury	0·999980
Residual mercury	1·000031

The probable error claimed is less than one part in a million.

Selenium, tellurium, antimony, and tin have all been used in the discharge tube, with no results of any value. This is unfortunate, for the atomic weight of selenium, 79·2, suggests that one of its isotopes must be an isobare of bromine or krypton; also the relation between tellurium and iodine is of great interest.

Iodine, fortunately, gave a very definite result. It is a simple element of atomic weight 127. This is rather surprising, for all the theoretical papers on the isotopic constitution of elements have predicted a complex iodine. Prophecy in physics becomes a difficult trade when experimental results produce these surprises, and apparently the only really trustworthy prediction is that there are plenty more in store for us.

The following is a list of elements and isotopes determined to date:—

Table of Elements and Isotopes.

Element	Atomic number	Atomic weight	Minimum number of isotopes	Masses of isotopes in order of their intensity
H	1	1·008	1	1·008
He	2	3·99	1	4
B	5	10·90	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22, (21)
Si	14	28·30	2	28, 29, (30)
P	15	31·04	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37, (39)
A	18	39·88	2	40, 36
As	33	74·96	1	75
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
I	53	126·92	1	127
X	54	130·32	5, (7)	129, 132, 131, 134, 136, (128, 130?)
Hg	80	200·60	(6)	(197–200), 202, 204

(Numbers in brackets are provisional only.)

By far the most important result of these measurements is that, with the exception of hydrogen, the weights of the atoms of all the elements measured, and, therefore, almost certainly of all elements, are whole numbers to the accuracy of experiment—namely, about one part in a thousand. Of course, the error expressed in fractions of a unit increases with the weight measured, but with the lighter elements the divergence from the whole-number rule is extremely small.

This enables the most sweeping simplifications to be made in our ideas of mass. The original hypothesis of Prout, put forward in 1815, that all atoms were themselves built of atoms of protyle, a hypothetical element which he tried to identify with hydrogen, is now re-established, with the modification that the primordial atoms are of two kinds—atoms of positive and negative electricity.

Although the latter unit has long been known to us as an "electron," its mate, which appears to be the real unit of mass, has only recently been given the name of "proton."

The Rutherford atom, whether we take Bohr's or Langmuir's development of it, consists essentially of a positively charged central nucleus around which are set planetary electrons at distances which are great compared with the dimensions of the nucleus itself. As has been stated, the chemical properties of an element depend solely on its atomic number, which is the charge on its nucleus expressed in terms of the unit charge e. A neutral atom of an element of atomic number N has a nucleus consisting of $K+N$ protons and K electrons, and around this nucleus are set N electrons. The weight of an electron on the scale we are using is 0·0005, so that it may be neglected. The weight of this atom will, therefore, be $K+N$, so that if no restrictions are placed on the value of K any number of isotopes is possible.

The first restriction is that, excepting in the case of hydrogen, K can never be less than N, for the atomic weight of an element is always found to be equal to, or greater than, twice its atomic number. The upper values of K also seem to be limited, for, so far, no two isotopes of the same element have been found differing by more than 10 per cent. of its mean atomic weight; the greatest numerical difference is eight units in the case of krypton. The actual occurrence of isotopes does not seem to follow any law at present obvious, though their number is probably limited by some condition of stability.

Protons and electrons may therefore be regarded as the bricks out of which atoms have been constructed. An atom of atomic weight m is turned into one of atomic weight $m+1$ by the addition of a proton *plus* an electron. If both enter the nucleus, the new element will be an isotope of the old one, for the nuclear charge has not been altered. On the other hand, if the proton alone enters the nucleus, and the electron remains outside, an element of next higher atomic number will be formed. If both these new configurations are possible, they will represent elements of the same atomic weight, but with different chemical properties. Such elements are called "isobares," and are actually known among the radio-active elements.

The case of the element hydrogen is unique, for its atom appears to consist of a single proton as nucleus with one planetary electron. It is the only atom in which the nucleus is not composed of a number of protons and electrons packed exceedingly close together. Theory indicates that when such close packing takes place the effective mass will be reduced, so that when four protons are packed together with two electrons to form the helium nucleus this will have a weight rather less than four times that of the hydrogen nucleus, which is actually the case.

It is not to be supposed that the whole-number rule is of exact mathematical accuracy, for the unit of the oxygen scale is a "packed" proton + an electron, and its value will certainly alter slightly with the degree of packing. On this account it is of the greatest importance to push the accuracy of methods of atomic weighing as far as possible, for variations from the whole-number rule, if they could be determined with precision, would give us some hope of laying bare that innermost of secrets, the actual configuration of the charges in the nucleus.

The results I have described lie on the borderline of physics and chemistry, and although as a chemist I view with some dismay the possibility of eighteen different mercuric chlorides, as a physicist it is a great relief to find that Nature employs, at least approximately, standard bricks in her operations of element-building.

Natural Camouflage.[1]

THE fine volume under notice is a new edition of the beautifully illustrated work which, originally appearing in 1909, first brought in a connected form before the public the many classical principles of concealing-coloration established by the genius of the American artist-naturalist Abbott H. Thayer. Important discoveries such as these, especially when the enthusiasm of their originator could recognise well-nigh no limits to their application, were bound to bring sharp differences of opinion. In America we have seen the rise of two rival camps, one, headed by the late Theodore Roosevelt, opposing the whole of Thayer's conclusions, the other accepting the whole and even interpreting the advertisement of Warning Colours and their simulation in Mimicry as examples of the working, in one form or another, of concealing-coloration.

In England, where, as the result of the writings of Wallace and Bates, and still earlier of Erasmus Darwin, the subject as a whole is older, an intermediate position has been taken. Here, naturalists recognise to the full the enduring value and fundamental importance of Thayer's discoveries, although believing that they do not offer a complete interpretation of animal colouring as a whole; and, in the beautiful frontispiece of the book, representing a peacock in the woods with its blue neck against the sky and posed so as to illustrate the conclusion that its pattern is "a marvellous combination of 'obliterative' designs, in forest-colors and patterns," in this and the flamingoes, and spoonbills with "the skies they picture" (plates viii–x), English naturalists

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[1] "Concealing-Coloration in the Animal Kingdom. An Exposition of the Laws of Disguise through Colour and Pattern: Being a Summary of Abbott H. Thayer's Disclosures." By Gerald H. Thayer. With an Introductory Essay by A. H. Thayer. New Edition with a New Preface. Illustrated by Abbott H. Thayer and Others, and with Photographs. Pp. xix+260+xvi plates. (New York: The Macmillan Co.; London: Macmillan and Co., Ltd., 1918.) 25*s*. net.